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(21) International Application Number: PCT/GB94/00301 (22) International Filing Date: 15 February 1994 (15.02.94) (30) Priority Data: 9302978.3 15 February 1993 (15.02.93) GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE IN HER BRITANNIC MAJESTY'S GOVERNMENT OF THE UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND [GB/GB]; Defence Research Agency, Farnborough, Hampshire GU14 6TD (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): DEAKIN, Martin, John [GB/GB]; 99 Dulverton Road, Ruislip, Middlesex HA4 9LE (GB). NICHOLLS, John, Rayment [GB/GB]; 8 The Green, Great Horwood, Buckinghamshire MK17 0RH (GB). (74) Agent: BECKHAM, Robert, William; Intellectual Property Dept., R69 Building, Defence Research Agency, Farnborough, Hampshire GU14 6TD (GB).		(81) Designated States: CA, GB, JP, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: DIFFUSION BARRIER LAYERS		
(57) Abstract A method of applying a continuous stable intermetallic diffusion barrier layer to a high temperature metallic article is described. In many instances, protective coatings are incompatible with the material of the substrate to which they are applied. Such incompatibility is overcome in the invention through <i>in situ</i> formation of an intermediate stable diffusion barrier layer by sequential deposition and subsequent reaction of suitable metals to form a continuous intermetallic layer. A conventional overlay coating may then be applied to the intermetallic layer without risk to the underlying substrate. The invention also contemplates creation of unitary diffusion barriers from multi-layer deposits; deposition of plural diffusion barriers, and formation of complete protective systems comprising substrate, diffusion barrier(s) and overlay coating prior to heat treatment <i>in situ</i> .		

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DIFFUSION BARRIER LAYERS

The present invention relates to protective coatings for metallic articles, and in particular to stable diffusion barrier coatings which can be applied to inhibit the deterioration of substrate materials as a result of interaction with external stimuli.

5

The utility of many materials is limited by their tolerance of operating conditions since, in hostile environments such as extended exposure to high temperatures and temperature cycling of the type found in gas turbine engines, environmental degradation can be very
10 severe.

Over the years, technology has developed a variety of protective e coatings to extend the operating lifetime and/or the maximum permitted working temperature of many materials. However, the coatings of
15 choice for particular applications, for example coatings having good oxidation or corrosion resistance, are not necessarily compatible with the substrate material to which they are applied. In many cases there are unfavourable interactions between the material of the substrate and the coating composition, with the result that the physical and
20 mechanical properties of the substrate are compromised. Deterioration of metallic materials is accelerated at elevated operating temperatures.

Formation of intermetallic protection layers of high temperature
25 components is known in JP 570155364, where a $PtAl_2$ discontinuous intermetallic phase of approximately 35-50 μ m is formed by a diffusion pack aluminising process at a temperature of 1150°C. High temperature materials are defined as those materials capable of operating at temperatures of 500°C or greater. This protection layer does not
30 afford uniform protection for the substrate material.

There is therefore a need for a uniform coating technique for high temperature components which will allow the best possible coatings for a given purpose to be applied to a particular substrate regardless of the interactions which might otherwise occur between the two.

5

According to the present invention, this is achieved by applying a stable continuous uniform diffusion barrier as an intermediate coating between the protective coating and the surface of the high temperature substrate material. The diffusion barrier serves to inhibit the
10 breakdown of the protective coating system by minimising coating/substrate interactions, such that efficacy of the protective coating is maintained even though the composition of the coating may be altered by loss through surface oxidation/corrosion. The diffusion barrier also helps to preserve the physical and mechanical properties
15 of the substrate, by limiting unfavourable interactions.

In particular, the inventive technique relies on the *in situ* formation of a continuous stable diffusion barrier by means of
20 sequential layering and subsequent reaction treatment of suitable metallic species to produce a diffusion barrier of intermetallic form. This inventive concept extends also to diffusion barriers consisting of multi-intermetallic layers each limiting the diffusion of a specific element (or elements), and is not necessarily limited to the
25 formation of a single intermetallic diffusion barrier layer of homogeneous structure. By selection of appropriate intermetallic species, interdiffusion of the protective coating through the barrier can be minimised.

30 The invention is a method of producing a continuous stable intermetallic diffusion barrier on a metallic high temperature article, the method comprising the steps of:

depositing at least a first layer of a first metal on the surface of the article;

- 5 depositing at least a second layer of a second metal on the surface of the article to a depth sufficient to provide a predetermined molar ratio of the first and second metals, and

- performing a reaction treatment which causes the first and second
10 metals to combine to form an intermetallic species.

The term metallic is used to define substrates made of metal, intermetallic or alloy materials.

15

For certain applications, it may be advantageous to use a number of sequential deposition steps to build up the requisite thickness of first and second metals prior to the reaction step.

- 20 As indicated above, it may sometimes be advantageous to deposit a plurality of intermetallic diffusion barriers, each of which serves as a barrier against diffusion by particular species.

- It is also possible to build up a complete protective system
25 comprising the metallic article substrate, diffusion barrier(s) and overlay coating prior to heat treatment *in situ* of the complete protective system. In this condition, it is important to ensure that the top-most metal of the diffusion barrier precursor has a low interaction with the overlay coating.

30

The reaction treatment step may be carried out prior to or during the normal alloy heat treatment cycle to which the metallic article is subject. Preferably the reaction treatment is a simple heating step which involves raising the deposited metals to a sufficiently high temperature to initiate the exothermic reaction necessary to form the intermetallic species. This may be performed under moderate vacuum to minimise depletion of the second metal layer by atmospheric oxidation.

Alternatively, the reaction treatment could be carried out at high pressure, for example using a hot isostatic pressing technique. Apart from simple heating, the reaction treatment step could also be performed by thermally exciting the first and second metal layers
5 using a laser beam, plasma treatment, or any other high energy surface treatment.

Preferably the diffusion barrier layer formed by the method of this invention is of a thickness between $0.1\mu\text{m}$ and $10\mu\text{m}$, although
10 more preferably the barrier layer thickness is between $0.8\mu\text{m}$ and $3.0\mu\text{m}$.

The invention will now be described by way of example with reference to Figure 1 which shows in schematic form the sequence of
15 steps necessary to carry out the invention.

Referring now to the Figure, step 1 represents the deposition of a first layer of a metal "A" upon the substrate. The thickness t_A of this first layer is determined by the overall thickness required for
20 the reacted thermal diffusion barrier coating and the stoichiometric proportion of metal "A" present within that coating.

Step 2 represents the deposition of a second metal "B" over the first layer deposited in step 1. Again, the thickness t_B of this
25 second layer is a function of the required thickness for the finished thermal diffusion barrier and the stoichiometric proportion of metal "B" present.

Step 3 represents the reaction treatment step which results in
30 combination of the two discrete layers of metals "A" and "B" into a single diffusion barrier layer of intermetallic "AB".

Assuming the reacted diffusion barrier layer A_xB_y is a stoichiometric intermetallic product, in order to obtain the desired
35 stoichiometry it must contain proportionally x moles of metal "A" and y moles of metal "B". If the respective atomic weights (M) of the two metals are M_A and M_B and their densities (p) are p_A and p_B , then the ratio of thicknesses t_A and t_B should be in the same ratio as:

$$\frac{x.M_A}{P_A} = \frac{y.M_B}{P_B}$$

This relationship assumes that thickness is directly proportional to
5 volume. It further assumes that little or no depletion of either
layer occurs due to solid/gas or solid/solid interactions. Where such
depletion occurs to an appreciable degree, appropriate adjustments
must be made to the relative thicknesses of the respective layer or
layers.

10

Example 1

The above technique has been successfully carried out on a
substrate of commercially available IMI834 titanium alloy. In this
case, a diffusion barrier was required to serve as an intermediate
15 layer between the substrate and an oxidation resistant coating. The
purpose of the oxidation resistant coating was to inhibit the ingress
of oxygen, thereby limiting the formation of a brittle α -case layer
which would otherwise severely reduce the mechanical properties of the
titanium substrate.

20

The sequence of steps outlined above was employed to form an
intermetallic $PtAl_2$ layer from the reaction of sequentially applied Pt
and Al layers using an R.F. biased D.C. sputtering route.

25 In order to minimise potential solid/solid interactions between
the substrate material and the first metal "A", particularly in view
of the high diffusivity of aluminium in titanium, the relatively slow
diffusing Pt layer was deposited first. This was followed by
deposition of the required thickness of Al in accordance with the
30 ratio:

$$\frac{M_{Pt}}{p_{Pt}} 2 \left(\frac{M_{Al}}{p_{Al}} \right)$$

(remembering that for $PtAl_2$, $x = 1$ and $y = 2$).

5

Depletion of the outer aluminium layer due to atmospheric oxidation was prevented by carrying out the reaction treatment in a moderate vacuum of roughly 2.0×10^{-5} bar. The reaction treatment in this instance consisted of heating for a period of 2 hours at a temperature of 750°C . X-ray diffraction analysis of the surface of the diffusion barrier coating confirmed that the desired $PtAl_2$ crystal morphology had been obtained.

The continuous $PtAl_2$ intermetallic layer thus formed was then overlay-coated with an 80/20 Ni/Cr oxidation resistant layer. An oxidative heat treatment for 100 hours in air at 700°C subsequently demonstrated the complete effectiveness of the $PtAl_2$ layer as a diffusion barrier for nickel. Moreover, etching of the substrate surface revealed no evidence of α -case formation, confirming the efficacy of the Ni/Cr layer as a barrier to oxidation.

Other intermetallics formed as diffusion barriers on IMI834 substrate are TiAl and $(PtTi_3 + TiAl)$. Nickel based substrates have also been subjected to the method of this invention, with each of NiCr, NiCrAl, NiAl and Ni having a diffusion barrier of $PtAl_2$.

Following diffusion barrier formation on the NiCr and NiAl substrates and application of an overlay coating system, each specimen was subjected to oxidative heat treatment for 80 minutes at 1050°C and also for 40 minutes at 1150°C . The $(PtTi_3 + TiAl)$ diffusion barrier on a substrate of IMI834 was subjected to an oxidative heat treatment of 700°C for 100 hours. Each of the treatments demonstrated the efficacy of the respective diffusion barrier layers.

Titanium aluminide alloys formed the substrate for intermetallic diffusion barrier layers of PtAl_2 and also TiAl .

The table below summarizes typical diffusion barrier formation for particular substrate materials, with associated typical thickness of diffusion barrier layers and also the efficacy testing conditions.

	Substrate	Diff. Barrier	Thickness range (total) μm	Stable exposure conditions
10	IMI 834	PtAl_2	0.7 - 3.2	Up to 100 hrs at 700°C
15	IMI 834	TiAl	1.9	-
	IMI 834	$(\text{PtTi}_3 + \text{TiAl})$	3.0	100 hrs at 700°C
20	a_2	PtAl_2	0.6 - 1.8	
	a_2	TiAl	1.9	
	NiCr	PtAl_2	1.8 - 4.0	80 mins/1050°C & 40 mins/1150°C
25	NiCrAl	PtAl_2	1.8 - 4.0	
	NiAl	PtAl_2	1.8 - 4.0	80 mins/1050°C & 40 mins/1150°C
30	Ni	PtAl_2	1.8 - 4.0	

From the examples it can be seen that a number of diffusion barrier intermetallics can be used for differing substrates. It will be understood that alternative oxidation resistant overlay coatings could have been used. It will also be appreciated that suitable
5 overlay coatings need not be confined to those imparting oxidation resistance.

CLAIMS

1. A method of producing a continuous stable intermetallic diffusion barrier on a metallic high temperature article, the method comprising the steps of:

depositing at least a first layer of a first metal on the surface of the article;

depositing at least a second layer of a second metal on the surface of the article to a depth sufficient to provide a predetermined molar ratio of the first and second metals, and

performing a reaction treatment which causes the first and second metals to combine to form an intermetallic species.

2. A method as claimed in claim 1 wherein a number of sequential deposition steps is employed to build up the requisite thickness of first and second metals prior to the reaction step.

3. A method as claimed in claim 1 or claim 2 wherein a plurality of sequential diffusion barriers of differing compositions is deposited to serve as barriers against diffusion by a variety of species.

4. A method as claimed in any preceding claim wherein the reaction treatment comprises heating the deposited layers to a temperature sufficient to effect exothermic reaction between the constituent metals of the or each diffusion barrier precursor.

5. A method as claimed in any preceding claim wherein the reaction treatment comprises thermal excitation of the deposited layers by high energy surface treatment such as laser beam or plasma treatment.

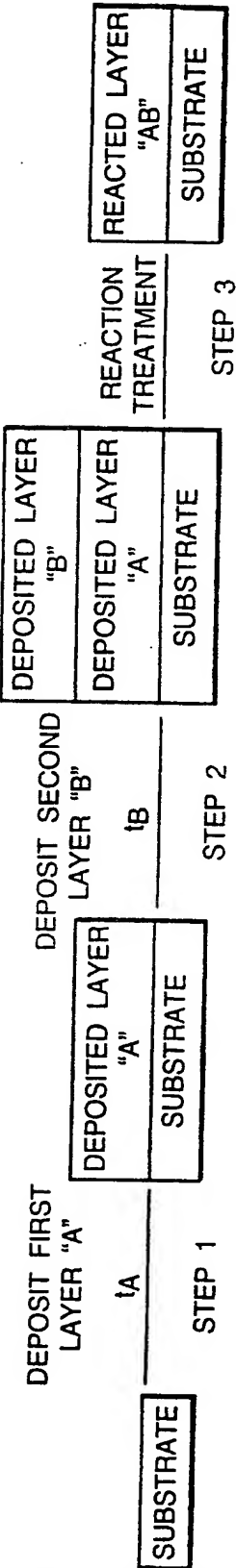
6. A method as claimed in any preceding claim wherein an overlay coating is applied to the outermost layer of the diffusion barrier or barriers prior to the reaction treatment step to form part of a complete protection system comprising the metallic article substrate, diffusion barrier(s) and overlay coating, which complete protection system is reaction treated *in situ*.

7. A method as claimed in any preceding claim wherein the reaction treatment step is carried out at non-ambient pressure.

8. A diffusion barrier or barriers produced by the method of any preceding claims having a total thickness of between 0.1 μ m and 10 μ m.

9. A diffusion barrier or barriers as claimed in claim 8 having a total thickness of between 0.8 μ m and 3.0 μ m.

Fig.1



t_A = THICKNESS OF LAYER "A"
 t_B = THICKNESS OF LAYER "B"

INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 94/00301

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C23C 30/00, B32B 15/01 // C23C 14/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B32B, C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG, WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE, A, 1900273 (E.I. DU PONT DE NEMOURS AND COMPANY), 21 August 1969 (21.08.69), page 5, line 1 - line 38 --	1,4
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A		1,4

☒ Further documents are listed in the continuation of Box C.

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European Patent Office, P.B. 5818 Patentaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

BENGT CHRISTENSSON

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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